UNIVERSITI PUTRA MALAYSIA

THE SYNTHESIS OF QUATERNARY AMMONIUM SALTS WITH CARBONYL FUNCTIONALITY AND STUDIES OF THEIR PHYSICAL PROPERTIES

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By

WONG CHAN HOONG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of Requirement for the Degree of Master of Science

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THE SYNTHESIS OF QUATERNARY AMMONIUM SALTS WITH CARBONYL FUNCTIONALITY AND STUDIES OF THEIR PHYSICAL PROPERTIES

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July 2002

Chairman: Associate Professor Karen Badri, Ph.D.

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This study is mainly focused on the synthesis of compounds of quaternary ammonium compounds. Iodoacetone has been produced through a simple method by reacting crystalline iodine and acetone in aqueous medium without adding any acid or base catalyst. Iodoacetone has been shown to react with various types of amines to produce tertiary and quarternary ammonium salts. For example, the reaction between pyridine and iodoacetone produced *N*-acetonyl pyridinium iodide. Iodoacetone reacts with triethylamine to produce *N*-acetonyl triethylammonium iodide and it reacts with triethanolamine to produce *N*-acetonyl triethanolamonium iodide. The reaction has been shown to be a general one. In many cases, single crystal x-ray analysis was used to solve the structure of the salts. We have found that the crystal system for *N*-acetonyltrimethylammonium iodide, *N*-acetonyltriethylammonium iodide, *N*-acetonylpyridinium iodide, 1-(1-ethyl-2-oxo-propyl)-pyridinium iodide and 2-hydroxy-

4,4-bis-(2-hydroxy-ethyl)-2-methyl-morpholin-4-ium iodide were monoclinic. Whereas *N*-acetonyltributylammonium iodide was tetragonal and *N*-acetonyltripropylammonium iodide was orthorhombic. The benefit in choosing crystalline iodine instead of other halogens as the reactant is mainly related to its low toxicity compared to chlorine and bromine. Surface tension measurements showed that for most of the salts synthesized performance as surface lowering agents were not very good. Nevertheless, *N*-acetonyltridodecylammonium iodide and *N*-acetonyltrihexyl-amonium iodide showed very low critical micelle concentration. Antibacterial and antifungal activity tests were also carried out on the quaternary ammonium compounds. We found that *N*-acetonyltrihexylammonium iodide was active against four types of bacteria namely *Bacillus subtilis* mutant, *Bacillus subtilis* wild type, Methicillin ressistant *Staphylococcus*, and *Pseudomonas aeruginosa*. The antifungal assay tested on three types of fungi; *Saccaromyces ceciricaee* (20341), *Candida albicans* (CA), and *Aspergillus ochraceous* (398). Only *N*-acetonyl tributhylamonium iodide and *N*-acetonyltrihexylamonium iodide were active against the fungi.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS GARAM KUATERNARI AMONIUM YANG MENGANDUNGI KUMPULAN BERFUNGSI KARBONIL DAN KAJIAN KE ATAS CIRI-CIRI FIZIKAL SEBATIAN

Oleh

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Pengerusi : Profesor Madya Karen Badri, Ph.D.

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Kajian ini adalah terutamanya memberi tumpuan ke atas penghasilan sebatian kuaternari ammonium. Iodoaseton telah dihasilkan melalui kaedah yang senang dengan menindakbalaskan hablur iodine dengan aseton dalam larutan akuas tanpa penambahan sebarang asid atau bes sabagai mangkin. Iodoaseton telah ditunjukkan dapat bertindakbalas dengan pelbagai jenis amina untuk menghasilkan garam kuaternari amonium. Sebagai contoh, tindak balas di antara piridin dan iodoaseton dapat menghasilkan *N*-asetonil piridinium iodida. Iodoaseton dapat bertindakbalas dengan trietilamina untuk menghasilkan *N*-asetonil trietilamonium iodida. Tindakbalas ini boleh dikatakan berlaku secara umum. Dalam banyak kes, analisis sinaran-X hablur telah digunakan untuk menyelesaikan strukur molekul untuk sebatian-sebatian itu. Kami telah mendapati bahawa sistem hablur untuk *N*-asetoniltrimetilamonium iodida, *N*-acetoniltrietilamonium iodida, *N*-asetonilpiridinium iodida, 1-(1-etil-2-okso-propil)-

piridinium iodida dan 2-hidroksi-4,4-bis-(2-hidroksi-etil)-2-metil-morfolin-4-ium iodida adalah monoklinik. Namun begitu, *N*-asetoniltributilamonium iodida adalah tetragonal dan *N*-asetoniltripropilamonium iodida adalah otorombik. Kebaikan dalam pemilihan hablur iodin dan bukannya halogen yang lain sebagai reaktan berkaitan terutamanya dengan ketoksikan yang rendah berbandingkan dengan klorin dan bromin. Penyukatan tegangan permukaan menunjukkan bahawa kebanyakan garam yang dihasilkan menunjukkan peranan sebagai ajen merendahkan tegangan permukaan yang sederhana. Walau bagaimanapun, *N*-asetoniltridodesilamonium iodida dan *N*-asetoniltriheksilamonium iodida telah menunjukkan nilai kepekatan kritikal misel (CMC) yang sangat rendah. Ujian aktiviti antibakteria dan antifungi juga dijalankan ke atas garam kuaternari amonium. Kami mendapati bahawa *N*-asetonilheksilamonium iodida adalah aktif dalam perencatan terhadap pelbagai jenis bacteria contohnya *Bacillus Subtilis* mutant *Bacillus Subtilis* jenis liar. Methicillin ressistant *staphylococcus* dan *Pseudomonas Aeruginosa*. Ujian antifungi telah dijalankan ke atas tiga jenis fungi *Saccaromyces cerevisiae* (20341) *Candida albicans* (CA) dan *Aspergillus ochraceous* (398). Hanya *N*-acetoniltributilamonium iodida dan *N*-asetoniltriheksilamonium iodida adalah aktif dalam merencat pertumbuhan fungi.

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I certify that an Examination Committee met on 17th July 2002 to conduct the final examination of Wong Chan Hoong on his Master of Science thesis entitled "Synthesis of Quaternary Ammonium Salts with Carbonyl Functionality and Studies of Their Physical Properties" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations that have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other at UPM or other institutions.

Wong Chan Hoong

Date:

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LIST OF ABBREVIATIONS

ATMAI	- N-Acetonyltrimethylammonium Iodide
ATEAI	- N-Acetonyltriethylammonium Iodide
ATPAI	- N-Acetonyltripropylammonium Iodide
ATBAI	- N-Acetonyltributylammonium Iodide
ATHAI	- N-Acetonyltrihexylammonium Iodide
ATDAI	- N-Acetonyltridodecylammonium Iodide
API	- N-Acetonylpyridinium Iodide
°C	- degree in Celsius
CHN	- Carbon, Hydrogen, Nitrogen Analyses
CMC	- Critical Micelles Concentration
δ	- chemical shift in ppm
d	- doublet
EIMS	- Electron Impact-Mass Spectroscopy
EOPPI	-1-(1-Ethyl-2-oxo-propyl)-pyridinium Iodide
FTIR	- Fourier Transfer Infra-Red
HEMI	- 2-Hydroxy-4,4-bis-(2-hydroxy-ethyl)-2-methyl-morpholin-4-ium Iodide
Hz	- Hertz
J	- Coupling constant in Hz
ml	- mililitre
m.p.	- melting point
MIC	- Minimum Inhibition Concentration
MPOB	- Malaysian Palm Oil Board

ORTEP	- Oak Ridge Thermal Ellipsoid Plot (from the program for Crystal Structure Illustration)
QAS	- Quaternary Ammonium Salt
NMR	- Nuclear Magnetic Resonance
s	- singlet
TLC	- thin layer chromatography
μg	- microgram
QAC	- Quaternary Ammonium Compounds
m	- multiplet

CHAPTER 1

INTRODUCTION

Halogenated Organic Compounds

Halogenated organic chemicals are important not only in themselves as finished products such as organochlorofluorocarbons, or precursors to finished products, such as polyvinylchloride, but also as intermediates for downstream products In the latter case this is so because a halogenated organic compound can undergo various reactions such as

Nucleophilic substitution

Dehydrohalogenation

Preparation of Grignard Reagents

Reduction

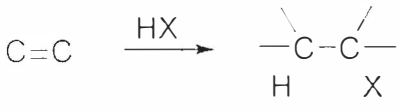
There are many methods available for synthesizing alkyl halides in the laboratory Most of these methods produce good yields of single products For example halogenated hydrocarbons are generally produced from the conversion of alcohols This reaction is generally satisfactory for the preparation of bromides and iodides Fiester *et al* 1961)

$$R\text{—}OH \xrightarrow{HX,\ PX_3} R\text{—}X \qquad [1]$$

Halogenated hydrocarbons can also be produced from alkanes using free-radical halogenation

[2]

Addition of hydrogen halides to alkenes will also produce halogenated hydrocarbons



[3]

(Wade, 1987)

Alkyl halides are versatile organic compounds, easily converted to most of the other functional groups. The most important property of alkyl halides is the ability of the halogen atom to leave with its bonding pair of electrons to form a stable halide ion. Many of the reactions of alkyl halides can be classified as eliminations or as nucleophilic substitutions. Some of these reactions are summarized in Table 1.1.

Table 1.1 Summary of Substitution and Elimination Reactions of Alkyl Halides

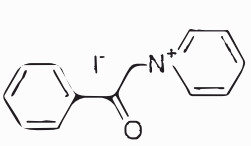
Nucleophile		*Product*	*Class of product*
R-X + - OH	→	R-OH	alkohol
R-X + - OR'	→	R-OR'	ether
R-X + - NH3	→	$R\text{-}NH^{+}{}_{3}X^{-}$	amine
R-X + $^{-}$:C≡C-R'	→	R-C≡C-R'	alkyne
R-X + $^{-}$:C≡N	→	R-C≡N	nitrile
R-X + R'-COO -	→	R'-COO-R	ester

Iodination of palmitic acid, PA, has been carried out in several solvent systems The two phase system composed of dichloroethane/ acetone/ water was found to be the preferred solvent (Muhammad *et al.*, 2000). Acetone was used to facilitate the reaction between iodine and palmitic acid. Iodoacetone was obtained as a side product or perhaps was an essential intermediate. This compound was also found to be highly reactive with tertiary amines forming quaternary ammonium salts

Therefore it was wise to focus on the reaction between acetone and iodine in an attempt to improve upon its synthesis. Several reaction conditions have been modified to obtain a better yield. Once an easy route to iodinated acetone was found, the technique was applied to other ketones. Compared to conventional quaternary ammonium compounds, the newly synthesized products with carbonyl functionality were considered as unique and perhaps possess several special properties.

In an investigation of the reaction of compounds containing a reactive hydrogen atom with iodine in the presence of a base, King *et al.* (1944 and 1946) attempted to make some aryl methyl ketones react with iodine and pyridine. They were able to prepare the substituted β-ketoalkylpyridinium iodides such as 1-phenacylpyridinium iodide (I), 1-(1-naphthoylmethyl)-pyridinium iodide (II). 1-(1-anthroylmethyl)-pyridinium iodide (III), and 1-(α-methylphenacyl)-pyridinium iodide (IV) These products were accompanied by some hydroiodide of the base as shown in reaction [4] In each of the reactions studied, approximately half of the iodine used appeared as pyridine

hydroiodide. Each of the substituted β-ketoalkylpyridinium iodides produced by the above reaction gave characteristic hydroxy acids when cleaved by means of aqueous alkali [5] (King *et al.*, 1945).



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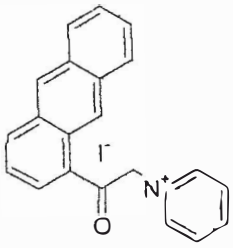

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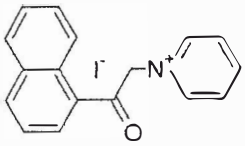

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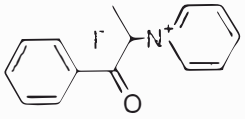

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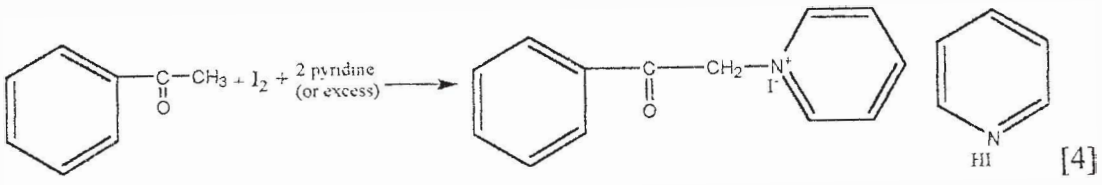
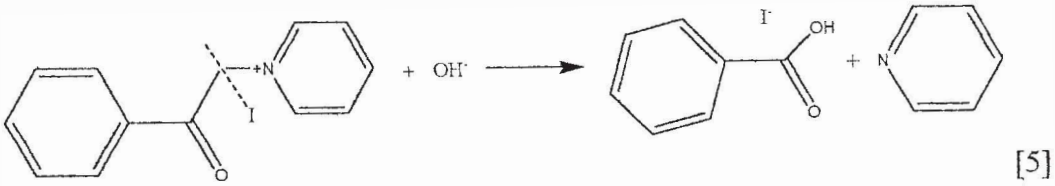


[4]



[5]